

## **MODIFIED POLYESTER FILAMENT, HETERO-SHRINKAGE CONJUGATE POLYESTER FILAMENT AND THEIR FABRICS**

### **Field of Invention**

This invention relates to a modified polyester filament, hetero-shrinkage conjugate polyester filament made by combining the modified polyester filament with high boiling water shrinkage filament and draw twisting, and their fabrics, especially to a polyester filament having 0.1~0.001 d.p.f. (denier per filament) ultrafine fluffs thereon, the filament obtained has soft, puffy, dry feeling and natural fiber like hand, can improve the deficiency of synthetic filament, elevate the commercial value of polyester filament, suitable to high grade clothing.

### **Prior Art**

Polyester can be widely used in versatile usages such as filament, film, packaging container and engineering plastics , wherein filament is the most used. Despite of polyester filament has excellent physical property, but also posses many deficiencies of synthetic fiber such as no water absorption, rough, no smooth hand etc., Especially in the clothing use, hand of fiber is the key point of commercial value. To improve the deficiencies of rough, no smooth hand, many recommendations have been provided. For example:

- (1) Japan patent publication 1964-29636, Japan laid open publication 1981-15411 and Japan laid open publication 1986-186576 discloses a manufacturing method by using two incompatible thermoplastic polymers to conjugate spinning , splitting to form ultrafine filament having soft hand.
- (2) Japan laid open publication 1989-91218 discloses a method by heterogeneously mixing a specific ethylene-vinyl acetate copolymer saponified product with a thermoplastic polyester resin just before spun, extruding from nozzles and subsequently subjecting the spun yarn to an alkali decrement treatment, the yarn obtained having a ramie-like feeling and a good touch.
- (3) Japan laid open publication 1989-91218 discloses a method by treating a hollow polyester filament containing a matting agent and a micropore-forming agent with an alkali, thereby forming specific micropores on the surface of said filament. The polyester yarn obtained having unique luster, dry feeling and excellent rebound elasticity.

produce an ultrafine polyester filament.

Furthermore, Japan patent publication 1972-11280 discloses a method to form long stripe micropore in the filament axis by extruding polyester filament containing polyalkylene ether of 0.4~5 % weight and alkali metal sulfonate of 0.3~3 % weight. The filament obtained has excellent water absorption. While Japan laid open publication 1979-101866 discloses a method by treating a polyester filament containing a metal salt of an organic sulfonic acid with an aqueous solution of an alkaline compound to remove the metal salt. Forming micropore thereon the filament surface. The filament obtained has excellent water absorption.

In the above mentioned prior arts, some arts can make filament having soft hand, some arts can make filament having dry touch feeling, some arts can improve polyester filament having appearance and touch feeling of natural filament, some arts can make filament surface forming long stripe micropore to improve water absorption of polyester filament. These only improve some characteristics locally but not all characteristics at the same time.

Besides, d.p.f. of filament can be decreased to reach the purpose of softening filament, for example: conjugate spinning method can be adopted in Japan patent publication 1964-29636, Japan laid open publication 1981-15411 and Japan laid open publication 1976-186576; Direct spinning fine denier filament method can be adopted in Japan laid open publication 1981-107006 and Japan laid open publication 1996-226013 to decrease d.p.f., the filament obtained has extreme soft hand feeling. But there are defects in these methods. Special conjugate spinning equipment should be used in conjugate spinning method, expensive cost is needed and chemical agent is needed in splitting. Direct spinning fine denier filament method under the actual production condition, d.p.f. of the filament obtained is greater than 0.1 denier. Though these two methods can be used to obtain filament having soft hand feeling, but the filament obtained is lack of dry feeling and touch as that of natural filament.

### **Summary of the Invention**

Accordingly, it is an object of the invention to provide a modified polyester filament having 0.1~0.001 d.p.f. (denier per filament) ultrafine fluffs thereon, the filament obtained has soft, puffy, dry feeling and natural fiber like hand, can improve the deficiency of synthetic filament made by prior art, elevate the commercial value of polyester filament, suitable to high grade clothing.

It is other object of the invention to provide fabric woven from modified polyester filament having 0.1~0.001 d.p.f. (denier per filament) ultrafine fluffs thereon has soft, puffy, dry feeling and natural fiber like hand.

It is another object of the invention to provide hetero-shrinkage conjugate yarn

by combining the aforementioned modified polyester with high boiling water shrinkage yarn to subject to draw twisting to get hetero-shrinkage conjugate yarn.

It is still another object of the invention to provide fabric woven from the afore-mentioned hetero-shrinkage conjugate filament and its textured yarn.

Modified polyester filament of this invention, which is formed by spinning the polyester resin composed of ethylene terephthalate more than 85 mol% as main component repeating unit, and component A organic sulfonate shown as the formula listed below



[ wherein R is selected from alkyl group of carbon 3 to 30, aromatic group and alkyl aromatic group of carbon 7 to 40; M is selected from alkali metal, alkali earth metal ] and component B polyalkylene glycol and satisfies the following three conditions

- (1) the content of said component A  $\text{RSO}_3\text{M}$  is from 0.4 weight% to 5 weight %;
- (2) the content of said component B polyalkylene glycol is from 0.4 weight% to 5 weight%;
- (3) said polyester filament obtained by spinning is subjected to alkali treatment to reduce the weight in an amount of 5-45% with 60~130°C alkali solution of concentration 0.2 to 8.0 weight%, dyeing to get polyester filament having 0.1~0.001 d.p.f. (denier per filament) ultrafine fluffs thereon

As to manufacturing method of modified polyester filament in this invention, the polyester used is mainly composed of polyethylene terephthalate, before the ending of esterification to polymerization, said component A  $\text{RSO}_3\text{M}$  in specified amount and said component B polyalkylene glycol in specified amount are added into the polyethylene terephthalate-based polyester to get the specified molecular weight polyester. This specified molecular weight polyester is subjected to melt spinning via extruder, drawing to form filament. Said polyester filament obtained by spinning and drawing is subjected to alkali treatment to reduce the weight and locally split the filament surface into fine denier filament, dyeing to get polyester filament having 0.1~0.001 d.p.f. (denier per filament) ultrafine fluffs thereon

As to manufacturing method of modified polyester filament in this invention, the

feature of key components A and B is long chain molecule. Component A organic sulfonate has no ester forming functional group, which is evenly distributed into inner part of filament in the manner of dispersion state. During the spin drawing process, organic sulfonate in the filament is drawn to form long shape mono-molecule by shearing force, and is parallel to the filament orientation axis to be evenly distributed into inner part of filament. During the subsequent alkali decrement treatment process, organic sulfonate molecules of said drawn and parallel to the filament orientation axis are dissolved, filament can be split into ultrafine fluffs. These ultrafine fluffs have uneven denier and uneven length, so soft, puffy, dry feeling and natural fiber like hand can be obtained. Component B polyalkylene glycol has ester forming functional group itself, which is evenly distributed into inner part of filament in the manner of dispersion state, but only a little portion for polymerization. These polyalkylene glycol can assist the dispersion of organic sulfonate in the filament, so can further enhance to split the filament.

Examples of the most used component A organic sulfonate that may be used to manufacture modified polyester filament in this invention are sodium, lithium, potassium and calcium salt of propyl sulfonic acid, butyl sulfonic acid; pentyl sulfonic acid, hexyl sulfonic acid, heptyl sulfonic acid, octyl sulfonic acid, nonyl sulfonic acid, sebacic sulfonic acid, lauryl sulfonic acid, myristic sulfonic acid; sodium, lithium, potassium and calcium salt of nonyl benzenesulfonic acid, lauryl benzenesulfonic acid, and mixtures of above mentioned organic sulfonate. Organic sulfonate used in this invention is not necessary a single compound, mixtures of above mentioned organic sulfonate can also be used, and do no good effect to this invention. The addition amount of organic sulfonate in this invention is in the range of 0.4~5.0 wt%. The effect reached is not obvious when the addition amount is less than 0.4 wt%. While if the addition amount is greater than 5.0 wt%, the effect reached is over saturated, the physical properties of filament obtained are decreased and unstable. The most suitable addition amount is up to the kind of organic sulfonate used.

Examples of the most used component B polyalkylene glycol that may be used to manufacture modified polyester filament in this invention are polyethylene glycol, polypropylene glycol polybutylene glycol, polyethylene glycol- polypropylene glycol copolymer. The addition amount of polyalkylene glycol in this invention is in the range of 0.4~5.0 wt%. The effect of promoting filament splitting is limited when the addition amount is less than 0.4 wt%. While if the addition amount is greater than 5.0 wt%, the effect of promoting filament splitting reached is over saturated, the heat resistance and physical properties of filament obtained are decreased. The molecule of polyalkylene glycol used is preferably in the range of 5,000 and 50,000. The effect of promoting filament splitting is limited when the molecule is less than 5,000. While if

the molecule is greater than 50,000, the thermal stability becomes bad and its compatibility with polyester is inferior to cause uneasy dispersion, and also do harm to the physical properties of filament. Polyalkylene glycol can copolymerize with polyester due to having two hydroxyl group. Polyalkylene glycol will be bound at the molecular chain of filament if polyalkylene glycol is completely copolymerize with polyester, and this will do harm to the effect of promoting dispersion of organic sulfonate and enhancing filament splitting. In view of the object of this invention, polyalkylene glycol preferably have only small portion to be linked with polyester and great portion to be dispersed into filament, so as to make use of effect of promoting dispersion of organic sulfonate and enhancing filament splitting. As to the reactivity of polyalkylene glycol, the reactivity of small molecular weight polyalkylene glycol is better due to the proportionality of polyalkylene glycol link onto polyester chain is higher ; the reactivity of high molecular weight polyalkylene glycol is bad due to the proportionality of polyalkylene glycol link onto polyester chain is lower. As to the compatibility of polyalkylene glycol with polyester, the compatibility of small molecular weight polyalkylene glycol is better, while the compatibility of high molecular weight polyalkylene glycol is bad. The higher the molecular weight of polyalkylene glycol, the more difficult to compatible with polyester, which do no good to the effect on dispersing organic sulfonate and enhancing splitting of filament. Besides, as to the heat resistance of polyalkylene glycol, the smaller the molecular weight of polyalkylene glycol, the better the heat resistance and the higher the molecular weight of polyalkylene glycol, the more inferior the heat resistance. In view of utility, the more the molecular weight of polyalkylene glycol will cause the defects of inferior heat resistance and bad physical properties. Take the compatibility, heat resistance and dispersion state in the polyester into consideration, preferable is the molecular weight of polyalkylene glycol in the range of 5,000~50,000, the most preferable is the molecular weight of polyalkylene glycol in the range of 10,000~30,000.

As to the addition means of said component A and B that may be used to manufacture modified polyester filament in this invention, component A and B can be added in the stage from esterification to the ending of polymerization in the polyester manufacture; or component A and B can be added in the stage of spinning to mix uniformly with polyester chip to be melt spun through extruder; or after component A and B are heated to melt and added in front of spinning head by metering pump, uniformly mixed by static mixer and then spun via spinneret. In view of the distribution evenness of component A and B in the filament, component A and B is preferably added in the process of polyester manufacture, more preferably in the stage from esterification to the ending of polymerization in the polyester manufacture.

As to manufacturing method of modified polyester filament in this invention, the polyester used is mainly composed of more than 85 mole% polyethylene terephthalate repeating unit, other dicarboxylic acids and diols can be added to co-polymerize without disturbing the advantageous effect of this invention. The other dicarboxylic acids used is aromatic dicarboxylic acid such as isophthalic acid, 5-sodium sulfonate isophthalic acid; aliphatic dicarboxylic acid such as adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid; cycloaliphatic dicarboxylic acid such as 1,4-hexahydrophthalic acid and lower esters of above mentioned dicarboxylic acids. Example of other diol ingredients that may be used to manufacture modified polyester filament in this invention are aliphatic diol such as 1,3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, isopentane diol; cycloaliphatic diol such as 1,4-cyclohexane diol, 1,4-cyclohexane dimethanol; aromatic diol such as p-dihydroxy benzene, 2,2-bis(4-hydroxybenzene)propane, bis-(4-hydroxybenzene) propane and their epoxy adducts. The above mentioned dicarboxylic acid and diol can be used one or more than one.

Alkali solutions used in the alkali decrement treatment are solutions of hydroxide of alkali metal and alkali earth, ammonium and tetraalkyl hydroxide. Examples of alkali hydroxide are sodium hydroxide, lithium hydroxide, potassium hydroxide. Examples of alkali earth hydroxide are magnesium hydroxide, calcium hydroxide. Examples of tetraalkyl hydroxide are ammonium tetramethyl hydroxide, ammonium tetraethyl hydroxide, ammonium tetrapropyl hydroxide, ammonium tetrabutylhydroxide. Preferably used is sodium hydroxide, lithium hydroxide.

The concentration used in the alkali decrement treatment is preferably in the range of 0.2~8 wt%. The decrement (reduction) speed is too slow if the concentration of alkali solution is less than 0.2 wt%; the decrement (reduction) speed is too rapid to control the reduction rate if the concentration of alkali solution is greater than 8 wt%, this will cause over reduction to greatly decrease the strength of filament. Working temperature of the alkali decrement treatment is preferably set in the range of 60~130 °C. The reduction speed is too slow and the reduction needed is too long if the temperature is lower than 60°C. The reduction speed is too fast to control the reduction rate if the temperature is higher than 130°C, this will cause over reduction to greatly decrease the strength of filament. The reduction rate is preferably set in the range of 5~45%. The effect reached is not obvious if the reduction rate is below 5%. The structure of filament will apt to be destroyed if the reduction rate is higher than 45%, this will cause the filament decrease its physical property rapidly and lose the utility. The concentration of alkali solution, temperature of alkali decrement treatment and reduction rate that can be suitably matched to get better effect depends on the kind and addition amount of above mentioned component A and B.

As to manufacturing method of modified polyester filament in this invention, additives such as matting agent, light stabilizer, light resistant, fluorescent whitening agent, antioxidant, anti-bacteria agent, deodorant, anti-static agent, defoaming agent, far infrared ray agent can be added as needed.

This invention will be understood more readily with reference to the following examples; however these examples are intended to illustrate this invention and are not to be construed to limit the scope of this invention. The addition amount used in the examples are expressed as parts by weight unless otherwise stated.

The analytical procedures used in this invention are described as follows.

a. IV ( intrinsic viscosity )

Measure the viscosity of polyester chip dissolved into mixture solution of phenol and 1,1,2,2-tetrachloroethane (weight ratio 3:2) at 30°C .

b. Fluffs on the filament surface

Observe the state of fluffs on the filament surface by using scanning electronic microscope (magnification: 1000~2000x).

◎ : excellent, ○: good, △: little fluffs, ×: almost no fluffs

c. Boiling water shrinkage:

Winding for 20 loops(20 meters) with hank reeling machine, and 1/30g per denier load hung below the filament tow, then recording the length  $L_1$  (cm) on square paper, and adequately binding the sample yarn, putting into 100°C boiling water for 30 minutes, taking the sample yarn out and drying naturally, measuring the length  $L_2$  of the filament tow hung with 1/30g per denier load. Boiling water shrinkage (%) =  $(L_1 - L_2)/L_1 \times 100$

### Example and Comparative example

#### Example 1

Add terephthalic acid 100 parts, ethylene glycol 60 parts in esterification vessel to undergo esterification at 250°C, 5 atm, decrease the pressure of esterification vessel gradually down to normal pressure to reach esterification rate 96% . Then add sodium pentadecanoyl sulfonate 2.3 parts, polyethylene glycol ( molecular weight 20,000) 2.3 parts, titanium oxide 0.46 parts, antimony acetate 0.046 parts, then transfer into polymerization vessel to undergo polymerization reaction to the expected torque of agitator at 285°C, vacuum degree below 1 torr. Polymer of IV 0.675 is extruded, water chilled and pelletized into chip. The modified polyester chip obtained is dried by normal crystallization, molten in the extruder to pass the circular orifice ( diameter : 0.25mm ) 36 orifices spinneret at 285°C for spinning. The spun filaments are air quenched, oiled and wound up by 2800 m/min to get undrawn filament. Then, the undrawn filament is drawn by ordinary method and heat treated to get 75d/36f drawn

filament of boiling water shrinkage 9% .Take this drawn filament as weft yarn and 75d/36f filament as warp yarn, woven to get 1/4 satin fabric. Treat the satin fabric by 85℃ 2% sodium hydroxide solution for alkali decrement treatment to reach reduction rate of 26% . Then, dye it by ordinary method with disperse dyestuff. The obtained fabric is observed by SEM ( Fig. 1 is the SEM photo before alkali decrement treatment; Fig. 2 is the SEM photo after alkali decrement treatment. Fig.3 is the SEM photo after alkali decrement treatment and dyeing.). Ultrafine fluffs can be found on polyester filament surface, the filament obtained has soft, puffy, dry feeling and natural fiber like hand.

Examples 2~6 and comparative examples 1~5

The kind and addition amount of component A and B in Example 1 are changed according to Table 1.

Table 1

	Component A		Component B		NaOH Concentration %	Reduction Temperature ℃	Reduction Rate %	Fluffs on the filament surface	Hand	Remark
	kind	Wt%	kind	Wt%						
Example 1	Sodium pentade-c anil sulfonate	2.0	PEG 20000	2.0	2.0	85	26.0	◎	○	
Example 2	Sodium pentade-c anil sulfonate	2.0	PEG 20000	2.0	1.0	85	12.5	○	○	
Example 3	Sodium pentade-c anil sulfonate	2.0	PEG 20000	2.0	0.5	110	15.0	○	○	
Comparative Example 1	Sodium pentade-c anil sulfonate	2.0	PEG 20000	2.0	5	120	48.5	◎	△	Strength of filament is low
Comparative Example 2	Sodium pentade-c anil	2.0	PEG 20000	2.0	0.15	60	4.5	X	X	



	sulfonate									
Comparative Example 3	Sodium pentadecanyl sulfonate	1.5	none	—	2.0	85	22.0	△~X	X	
Comparative Example 4	Sodium lauryl sulfonate	1.5	PEG 600	2.0	2.0	85	23.1	△	X	
Example 4	Sodium lauryl sulfonate	3.0	PEG 20000	1.0	3.0	95	35.6	◎	○	
Example 5	Sodium lauryl sulfonate	2.0	PEG 10000	3.0	0.8	75	18.3	◎	○	
Example 6	Sodium lauryl sulfonate	3.5	PEG 30000	1.5	1.2	75	28.6	◎	○	
Comparative Example 5	Sodium lauryl sulfonate	5.5	PEG 10000	5.5	1.2	85	39.7	◎	○	

Note: Fluffs on the filament surface is evaluated by ◎: excellent, ○: good,

△: little fluffs, ×: almost no fluffs.

◎: Hand is evaluated by ○: excellent, △: fair, ×: bad.

#### Example 7

The modified polyester in Example 1 is subjected to the spinning method of Example 1 to get undrawn filament. The undrawn filament is draw twisted by false twister to get textured yarn of 75d/36f. Weaving, alkali decrement treatment and dyeing are undergone according to steps as described in Example 1. Ultrafine fluffs can be found on polyester filament surface, the filament obtained has soft, puffy, dry feeling and natural fiber like hand.

#### Example 8

Combine the undrawn filament of Example 7 with a high boiling water shrinkage filament (boiling water shrinkage 20%) and draw twist according to the method described in Example 7 to get hetero-shrinkage conjugate yarn of 105d/48f. Weaving, alkali decrement treatment and dyeing are undergone according to steps as described in Example 7. Ultrafine fluffs can be found on polyester yarn surface of the woven

fabric, the yarn obtained has soft, puffy, dry feeling and natural fiber like hand.

#### Example 9

Combine the undrawn filament of Example 1 with a high boiling water shrinkage filament (boiling water shrinkage 20%) and draw twist according to the method described in Example 1 to get hetero-shrinkage conjugate yarn of 105d/48f. Weaving, alkali decrement treatment and dyeing are undergone according to steps as described in Example 1. Ultrafine fluffs can be found on polyester yarn surface of the woven fabric, the yarn obtained has soft, puffy, dry feeling and natural fiber like hand.

#### **Brief Description of the Drawings**

Fig. 1 is the SEM photo before alkali decrement treatment.

Fig. 2 is the SEM photo after alkali decrement treatment.

Fig. 3 is the SEM photo after alkali decrement treatment and dyeing.